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WATER QUALITY BASIC DATA. REPORT ON ANALYTICAL REFERENCE SAMPLE TYPE I, BD-2

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

August 1958

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WATER QUALITY BASIC DATA

Report on

ANALYTICAL REFERENCE SAMPLE
TYPE I, BD-2

August, 1958

U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

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PARTICIPANTS IN STUDY OF SAMPLE TYPE I, BD-2

(Distributed April 4, 1958)

City of Buffalo, Division of Water
Buffalo, New York

Erie County Department of Health
Buffalo, New York

East Liverpool Water Department
East Liverpool, Ohio

City of Memphis
Light, Gas & Water Division
Memphis, Tennessee

North Augusta Filter Plant
North Augusta, South Carolina

Chemical-Toxicological Laboratory
Louisiana State Health Department

City Water Company, Plant #9
Chattanooga, Tennessee

Tennessee Valley Authority
Stream Pollution Control Laboratory
Chattanooga, Tennessee

Cairo Water Company
Cairo, Illinois

Evansville Water Department
Evansville, Indiana

Easton, Pennsylvania Water Dept.
Easton, Pennsylvania

Burlington Municipal Water Works
Burlington, Iowa

Crown Zellerbach Corporation
Central Research Department
Camas, Washington

Lawrence Experiment Station
Lawrence, Massachusetts

East St. Louis Water Company
East St. Louis, Illinois

Board of Public Utilities
Kansas City, Kansas

City of Dubuque Water Department
Dubuque, Iowa

Yankton Water Department
Yankton, South Dakota

City of El Paso Water Treatment Plant
El Paso, Texas

Missouri Utilities Company
Cape Girardeau, Missouri

Arizona Water Company
Yuma, Arizona

Union Bag-Camp Paper Corporation
Savannah, Georgia

INTRODUCTION

Since the initiation of the Water Quality Basic Data Program in October of 1957, analytical data are being accumulated in a steadily increasing volume. Because these analyses originate from so many different laboratories, it is essential that they be comparable as to precision and accuracy. The reference sample technique is a mechanism by which this objective can be achieved. Reference samples will be submitted to each of the collaborating laboratories at periodic intervals to insure continued precision and accuracy of the data submitted.

REPORT ON THE ANALYTICAL REFERENCE SERVICE SAMPLE TYPE I, BD-2

Sample Type I, BD-2 is the second in a series of standard samples representative of the mineral analyses being reported to the Water Quality Basic Data Program by the laboratories cooperating in this activity. These determinations include most of the tests commonly used in the chemical and physical characterization of waters. Most laboratories have little or no difficulty in performing these examinations, as attested by the overall excellence of the reported results.

The individual laboratory results are presented in Table I, and the bar graphs. The dotted lines on the graphs represent the limits of acceptability for the individual tests. The selection of the limits of acceptability were influenced by the precision with which each test can be performed, as determined by "Standard Methods" as well as needs of the Water Quality Basic Data Program. Results falling outside the acceptable range were not used in the subsequent statistical calculations because it is believed that these values were influenced by major errors in method, such as improperly standardized reagents, incorrect calculation, or manipulative errors. In most cases, those laboratories whose results were outside the acceptable range were notified immediately and requested to review the procedure used in order to determine the cause of discrepancy.

It is strongly urged that all cooperating laboratories furnish comments on the analytical methods used. A complete log of pertinent details, difficulties, modifications, sources of error, and other factors affecting the precision and accuracy of the analytical procedures would be extremely valuable in the development of simpler and more accurate analytical procedures. This report may also be useful as a means of self-evaluation by each of the participating agencies. Assistance on laboratory procedures is available to the cooperating laboratories from the Public Health Service, through its Regional offices or the Sanitary Engineering Center.

DISCUSSION OF RESULTS

The statistical parameter used in this report is the standard deviation, $\bar{S}$, as calculated according to the formula:

$$\bar{S} = \sqrt{\frac{\Sigma d^2}{n}}$$

where d = deviation of an individual result from the amount added.

n = number of results used in the calcaulations.

Only those results falling within the range of acceptability for the particular test were used in the calculation of the standard deviation.

CHLORIDE

Although several methods are available for this determination, 17 of the 18 results used in the calculations are obtained using the Mohr procedure. The most frequent criticism of this method is the obscurity of the real endpoint. However, this can be easily corrected by the use of a suitable titration blank. The chief precaution to be observed in this determination, as in any volumetric procedure, is standardization of the reagents. Fourteen of the 18 laboratories reporting this analysis fell within $\pm$ 10% of the known value. The standard deviation calculated for this group is 2.5 mg/l. It is evident that most laboratories can easily perform the chloride determination within the limits of precision desired. Those falling outside these limits should review their procedures to determine the possible sources of error and to make the necessary corrections.

SULFATE

Eight of the 11 laboratories reporting this analysis fell within $\pm$ 10% of the known value. The standard deviation calculated for this group was 7.1 mg/l. Of the three laboratories outside the range, one reported using the gravimetric procedure; one reported using the turbidimetric procedure, and the third did not report the procedure used.

From this set of data, it is not possible to point out a superiority of one procedure over the other. It is our experience, however, that the gravimetric procedure is more accurate than the turbidimetric, while the latter procedure has much to recommend it because of the simplicity and speed with which the method is carried out.

On this particular sample, using either procedure, it was necessary to remove all of the turbidity prior to sulfate precipitation. If this operation was not properly performed, a high result would be obtained. The usual precautions of washing and drying precipitates also had to be observed to obtain good result on the gravimetric procedure.

TOTAL DISSOLVED SOLIDS

In the performance of the Total Dissolved Solids determination, no difficulties should normally be encountered. A measured volume of turbidity-free sample is merely placed in a dish, evaporated to dryness and weighed. Two precautions must be observed: the turbidity must be completely removed, and the sample must be taken to dryness at 103-105^{o}C. Incomplete drying allows water of hydration to be included in the final weighing which, along with turbidity particles, can cause a result in excess of the true amount. A third precaution, also related to drying, must be exercised. If the drying temperature is too high, certain materials such as carbonates, bicarbonates, or chlorides may be volatilized and the resulting figure will be too low. For these reasons, the precautions, while simple, must be strictly observed.

Assuming no great variation in the drying temperature, the precision of this test is dependent primarily on the precision of the weighing operation. The standard deviation for this operation has been determined by "Standard Methods" as 0.9 mg/l (page 270). Assuming a 100 ml sample was used, then a variation of 18 mg/l may be expected for 95% of the results. (0.9 x 10 x 2). On this basis, a variation of 10% of the true value should not be too difficult to achieve. Only one of the 13 laboratories reporting this analysis fell outside the 10% limits. The standard deviation calculated for this series was 19.9 mg/l.

A word of caution should be noted here. The size of sample taken for this test will influence its precision considerably, particularly with waters

of low solids content. To achieve a satisfactory precision, the sample size should be large enough to produce a residue weighing not less than 20 mg in order that the precision of the weighing fall within 10% of the true value.

ALKALINITY

This volumetric procedure allows a choice of indicators or electrometric measurement for the detection of the end point. Six laboratories reported using methyl orange, four used methyl purple, two used mixed indicator and one used the pH meter. Of the 18 laboratories reporting, 14 fell within 10% of the true value. Of the four laboratories outside the acceptable range, three reported using methyl orange. The standard deviation, calculated from the 14 acceptable values was 4.2 mg/l.

HARDNESS

All laboratories employed some modification of the EDTA titration procedure. One laboratory also reported a parallel titration by the soap method. Fourteen of the 18 laboratory results fell within 10% of the concentration added to the sample. The standard deviation for this group was 6.7 mg/l. This titration presents no great difficulty as the endpoint is easy to detect, provided that the indicator, Eriochrome Black T, is in good condition. Errors may have been due to improperly standardized reagent, miscalculation, or poor indicator. "Standard Methods" indicates that a precision of $\pm$2 mg/l is easily attainable for the hardness range used in this sample.

HYDROGEN ION CONCENTRATION (pH)

The true pH of this sample is the resultant of the various chemicals added to distilled water to make up the desired concentrations of the ions being tested. This value cannot be readily calculated, therefore, the value reported under amount added represents the result obtained at the SEC using a carefully standardized instrument, immediately after the sample was prepared. Some variation from this value would be expected among the different laboratories since the stability of the solution would be affected by transportation and by the exposure to air during subsequent handling. Twelve of the 18 laboratories reported within 0.2 pH unit of the value observed at SEC. The greatest

deviation was 0.6 units, reported by one laboratory. "Standard Methods" indicates that a precision of 0.1 pH unit is readily attainable with the glass electrode. It does not consider the colorimetric methods as suitable for pH measurement of water and recommends that they be used only to obtain a rough approximation of the true pH value. Of the seven laboratories that reported using colorimetric methods, two were outside the range of 0.2 pH units.

TURBIDITY

The results of this test were very discouraging. A large part of the trouble may have been due to the method of preparation of the standard sample. It was observed that after long standing the turbidity particles tended to agglomerate, thus reducing the observed turbidity value. Only six of the laboratories reported results within 20% of the added value. Most of the other results were much lower, tending to confirm the above observation. However, incomplete shaking of the sample could also account for this large error. Another source of error may be the conversion to Jackson Units when instruments other than the Jackson Candle turbidimeter are used. The problem of particle agglomeration is being studied. It is expected that this will be solved before the next reference sample is issued, so that a more reliable evaluation of the turbidity measurements can be made.

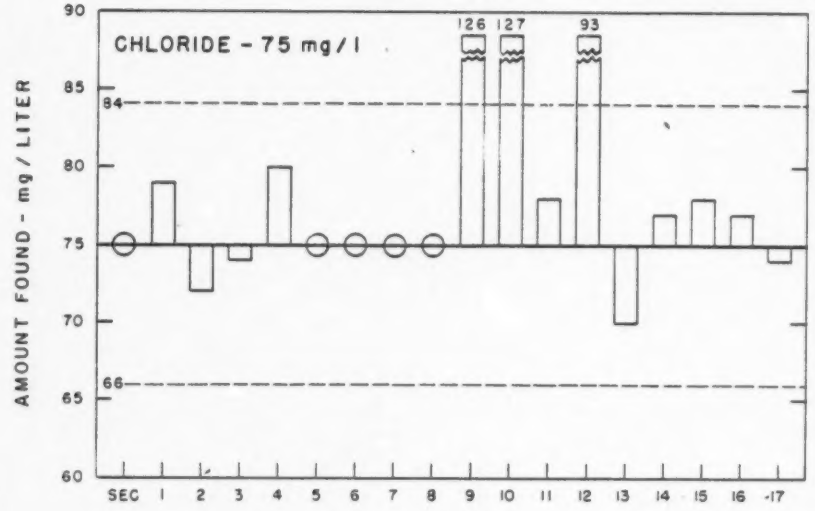
TABLE I - SUMMARY OF RESULTS
ANALYTICAL REFERENCE SAMPLE TYPE I, BD-2

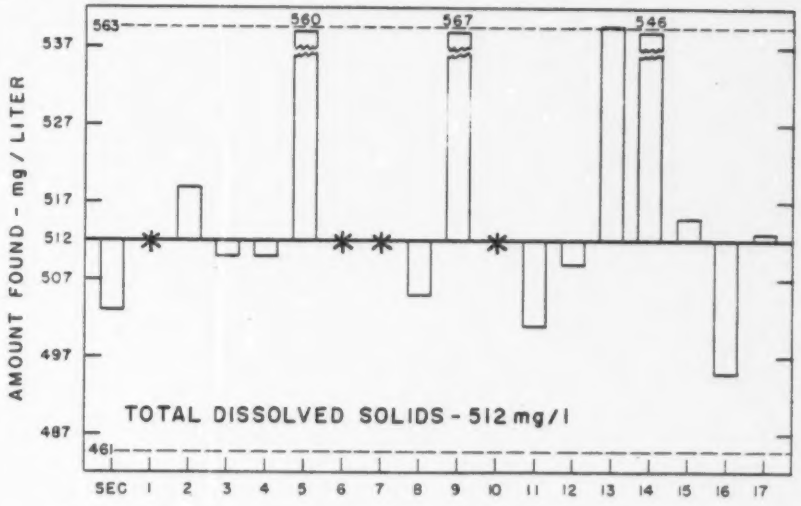
Analyses Performed	Chloride	Sulfate	T.D.S.	Alkalinity	Hardness	pH	Turbidity
Amount Added	75 mg/l	180 mg/l	512 mg/l	80 mg/l	188 mg/l	8.0	81 Jackson Units
	Average Amount Reported by Each Laboratory						
Lab. #							
1	79	-	-	86	198	7.9	37
2	72	-	519	80	221*	8.1	61
3	74	181	510	83	196	8.1	78
4	80	175	510	90*	192	7.8	52
5	75	185	560	82	197	8.1	95
6	75	-	-	88	194	7.6	50
7	75	-	-	78	101*	7.9	25
8	75	177	505	86	188	8.3	64
9	126*	114*	567*	76	196	8.3	160
10	127*	-	-	100*	210 299*	7.8	76
11	78	192	501	80	197	7.9	100
12	93*	169	509	80	190	7.9	66
13	70	244*	540	89*	190	7.7	26
14	77	181	546	88	140*	8.1	-
15	78	-	515	77	193	7.5	25
16	79	189	495	93*	199	7.4	79
17	74	254*	513	81	194	7.9	29
18	129*	-	-	83	186	7.8	73
19	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-
SEC*	75	187	503	83	189	8.0	81
$\bar{S}$	2.5	7.1	19.9	4.2	6.7	-	-

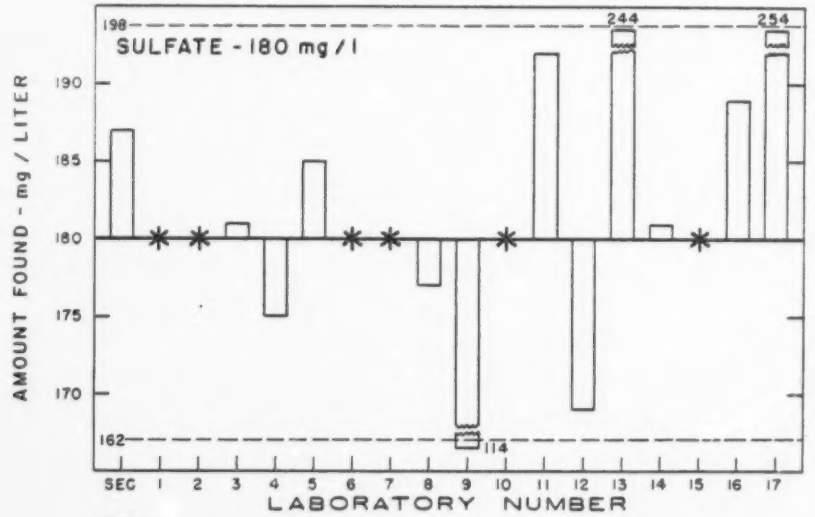
* Results not used in calculation of Standard Deviation.....

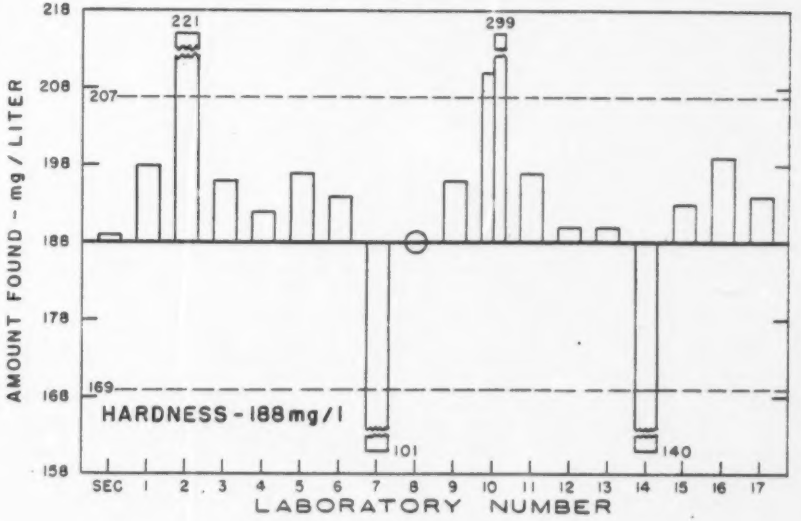
WATER QUALITY BASIC DATA

ANALYTICAL REFERENCE SERVICE SAMPLE TYPE I, BD-2









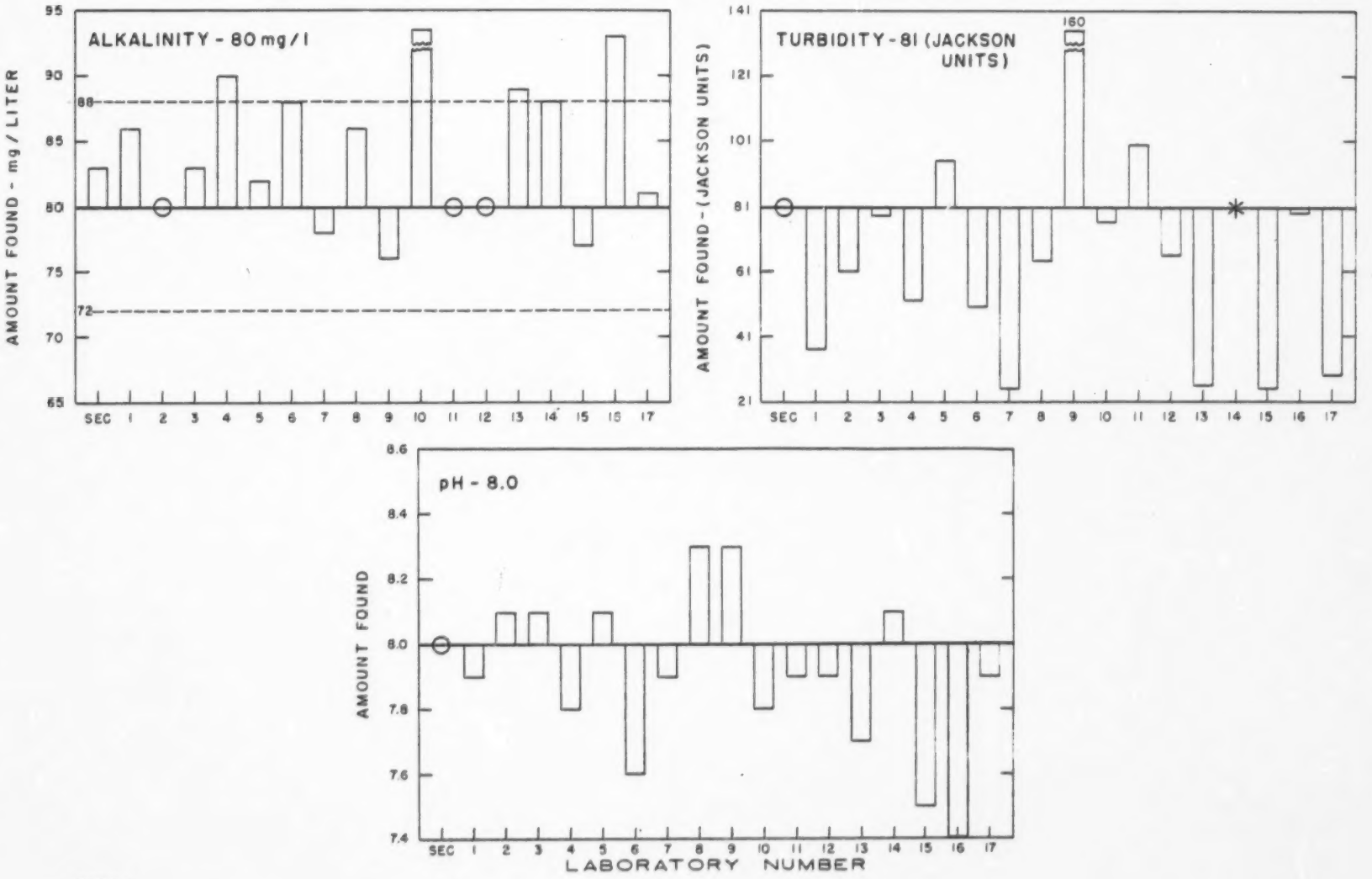
NOTE:

○ - PERFECT RESULTS

✱ - NO ANALYSIS PERFORMED

WATER QUALITY BASIC DATA

ANALYTICAL REFERENCE SERVICE SAMPLE TYPE I, BD-2



NOTE:

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